09/762847
JC02 Rec'd PCT/PTO 09 FEB 2001

Odorization of gas

The present invention relates to the odorization of gas.

Town and coke-oven gases obtained by thermal processes contained intensely odoriferous components and therefore had a strong intrinsic odour, so that escaping gas could be readily detected.

Because of its origin (natural gas) and a relatively high degree of purity, the gas used nowadays in the public network is in itself virtually odourless; if leakages are not noticed in good time, explosive gas/air mixtures with a high hazard potential quickly form. For safety reasons, gas is therefore odorized by adding odorants. For example, in Germany it is stipulated that all gases which do not have sufficient intrinsic odour and are distributed in the public gas supply (DVGW-Arbeitsblatt [Worksheet] G 260) are odorized in accordance with DVGW-Arbeitsblatt [Worksheet] G 280; DVGW = Deutscher Verein des Gas- und Wasserfaches e.V. [German Association on Gas and Water], Eschborn. These odorizing compositions are detectable even when highly diluted and, because of their extremely unpleasant odour, act, as is desired, as a warning signal for people. In Germany, approximately 90% of service gas is currently odorized with tetrahydrothiophene (THT) (12-25 mg/m^3); in addition, odorization using mercaptans or thioethers is also customary.

THT and mercaptans are highly suitable for reliable odorization of gas. However, in the context of treating the environment with more respect, it is to be noted that during the combustion of such odorized gases, sulphur dioxide forms as combustion product – only in small amounts at each individual combustion site, but, viewed on a countrywide scale, in amounts of a few hundred tons per year. It would be desirable to overcome this disadvantage; however, a number of requirements have to be satisfied:

1. The odour must be unpleasant and unmistakable (odours from kitchens and homes are excluded). It must act as a warning signal for people who smell escaped gas.

2. Everybody with an average sense of smell and average physiological condition must be able to detect the odour.

3. The warning odour stage (= average odour intensivity) must be achieved before the ignition limit or a kinetic carbon monoxide content is reached.

4. The odorizing composition must be as nontoxic as possible and must not form any toxic combustion products.

5. The odorizing composition must have high volatility and evaporate leaving as little residue as possible.

6. A suitable odorizing composition must not condense at winter temperatures, nor separate, nor adhere to metallic pipes.

7. The odorizing composition must combust without leaving a residue.

8. The odorizing composition must be storage-stable and chemically resistant to the gas and to the plants. It must not promote corrosion, nor attack customary seals.

Attempts have already been undertaken to provide new gas odorizing compositions. Thus, the following, for example, have been proposed:

- alkyl acrylates, vinyl or alkyl ethers and mixtures thereof (JP 76-7481),

- n-valeric acid, optionally in combination with ethyl acrylate and/or triethylamine (JP 76-34 841),

- ~~mixtures of sulphur compounds and aliphatic aldehyde (JP 78-35 562),~~

- cycohexene (JP 83-42 235),

- norbornene derivatives (JP 87-1998) and

- saturated ethers, saturated esters, and mixtures thereof with mercaptans.

It has now been found that, by additions of

A. acrylic C_1-C_{12}-, preferably C_1-C_8-alkyl, esters,

B. nitrogen compounds and optionally

C. antioxidants

progressively odorized gas is obtained which largely combines the desired properties. The novel odorizing composition can be added to the gas in the same order of magnitude as sulphur-containing compounds and does not produce corrosion-promoting products upon combustion.

The acrylic esters A include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert-butyl acrylate, pentyl acrylate, hexyl acrylate, heptyl acrylate, octyl acrylate and dodecyl acrylate. In a preferred embodiment, mixtures of acrylic C_1-C_6-alkyl esters are used as component A; a particularly preferred combination comprises methyl acrylate and ethyl acrylate alongside one another. The acrylate mixtures can contain the lower and the higher esters in each case in the weight ratio of from 9:1 to 1:9, preferably 7:3 to 3:7.

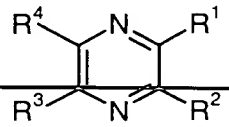
Preferred nitrogen compounds B include primarily compounds

- with a flash point above 20°C, preferably above 40°C (measured in accordance with ISO 2719),
- with a molecular weight of from 80 to 160, preferably 110 to 145,
- with a boiling point of from 90 to 210, preferably 110 to 165°C.

The nitrogen compounds B include, for example,

lactones, such as caprolactone

nitriles, such as 2-nonenenitrile and compounds of the formula



(I)

where

R^1 to R^4, independently of one another, are hydrogen or C_1-C_4-alkyl, preferably methyl or ethyl.

Preferred compounds (I) are e.g. 2-methylpyrazine, 2,3-dimethylpyrazine, 2,6-dimethylpyrazine, 2,3,5-trimethylpyrazine, tetramethylpyrazine, 2-ethylpyrazine, 2,3-diethylpyrazine, 5,2-methylethylpyrazine, 2,3-methylethylpyrazine, 5,2,3-methyldiethylpyrazine and 3,5,2- and 3,6,2-dimethylethylpyrazine. 2,3-methylethylpyrazine and tetramethylpyrazine are preferred.

The nitrogen compounds B can be used in amounts of from 1 to 100, preferably 30 to 100, in particular 10 to 50, parts by weight per 1 000 parts by weight of A.

To protect against undesired oxidation, the odorizing compositions may comprise antioxidants, as are described, for example, in Römpp-Lexikon Chemie Version 1.3. Preferred antioxidants include butylhydroxyanisole, ionol = tert-butylhydroxytoluene, hydroquinone monomethyl ether and α-tocopherol.

The antioxidants C are preferably used in amounts of from 0.01 to 5, in particular 0.05 to 2, especially 0.1 to 1, parts by weight per 1 000 parts by weight of A.

Preferred gas odorizing compositions can, for example, have the following compositions:

Example 1

Ethyl acrylate	600 g
Methyl acrylate	360 g
5,2,3-Methyldiethylpyrazine	39 g
Ionol	1 g

Example 2

Ethyl acrylate	535 g
Methyl acrylate	400 g
2-Methylpyrazine	64 g
Ionol	1 g

Example 3

Ethyl acrylate	320 g
Methyl acrylate	637 g
3,5(6),2-Dimethylethylpyrazine	42 g
Ionol	1 g

Example 4

Ethyl acrylate	460 g
Methyl acrylate	460 g
2,6-Dimethylpyrazine	79 g
Ionol	1 g

Example 5

Ethyl acrylate	520 g
Methyl acrylate	459 g
2,3,5-Trimethylpyrazine	20 g
Ionol	1 g

Example 6

Ethyl acrylate	885 g
Methyl acrylate	100 g
2,3-Methylethylpyrazine	14 g
Ionol	1 g

Example 7

Ethyl acrylate	700 g
Methyl acrylate	274 g
2,3-Dimethylpyrazine	25 g
Ionol	1 g

Example 8

Ethyl acrylate	350 g
Methyl acrylate	600 g
Tetramethylpyrazine	49 g
Ionol	1 g

Example 9

Ethyl acrylate	144 g
Methyl acrylate	800 g
2-Ethylpyrazine	56 g

Example 10

Ethyl acrylate	615 g
Methyl acrylate	300 g
5,2-Methylethylpyrazine	85 g

Example 11

Ethyl acrylate	320 g
Methyl acrylate	649 g
3,5(6),2-Dimethylethylpyrazine	15 g
2,3-Dimethylethylpyrazine	15 g
Ionol	1 g

Example 12

Ethyl acrylate	120 g
Methyl acrylate	807 g
2-Ethylpyrazine	30 g
5,2-Methylethylpyrazine	42 g
Ionol	1 g

Example 13

Ethyl acrylate	520 g
Methyl acrylate	434 g
2,6-Dimethylpyrazine	20 g
2,3-Methylethylpyrazine	25 g
Ionol	1 g

Example 14

Ethyl acrylate	320 g
Methyl acrylate	633 g
2,3-Diethylpyrazine	34 g
2,3-Methylethylpyrazine	12 g
Ionol	1 g

Example 15

Ethyl acrylate	759 g
Methyl acrylate	200 g
2-Methylpyrazine	30 g
Tetramethylpyrazine	10 g
Ionol	1 g